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Targeted pre-treatment of hemp bast fibres for optimal performance in biocomposite materials: A review

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Abstract

Global interest in the use of plant fibres in natural fibre reinforced composites (NFCs) is growing rapidly. The increased interest is primarily due to the advantageous properties of natural fibres including biodegradability, low cost, low density and high stiffness and strength to weight ratio. In order to achieve strong NFCs, well separated and cellulose-rich fibres are required. Hemp is taking a center stage in this regard as a source of suitable natural plant cellulose fibres because natural hemp bast fibres are long and inherently possess high strength. Classical field and water retting methods have been used for centuries for removal of non-cellulosic components from fibrous plant stems including from hemp, but carries a risk of reducing the mechanical properties of the fibres via damaging the cellulose. For NFCs new targeted fibre pre-treatment methods are needed to selectively and effectively remove non-cellulosic components from the plant fibres and for producing cellulose rich fibres without introducing any damage to the fibres. A key feature for successful use of natural fibres such as hemp fibres in composite materials is optimal interfacial contact between the fibres and the hydrophobic composite matrix material. Targeted modification of natural fibres for NFCs must also be targeted to optimize the fibre surface properties. Consequently, improved interfacial bonding between fibres and hydrophobic polymers, reduced moisture uptake, increased microbial degradation resistance, and prolonged durability of NFCs can be achieved. This review, using hemp bast fibres as an example, critically and comprehensively assesses the targeted pretreatment technologies and data available for producing well separated cellulose bast fibres having optimal chemical and physical properties for maximizing the mechanical performance and durability of NFCs.

Keywords: Hemp fibres; mechanical properties; stiffness; tensile strength; natural-fibre composites

1. Introduction

Natural plant fibres such as hemp and flax fibres are currently receiving high research attention for use as reinforcing agents in composites to substitute for synthetic fibres (Fuqua et al., 2012; Joshi et al., 2004; Liu et al., 2016; K. L. Pickering et al., 2007; Van Vuure et al., 2015). Hemp (*Cannabis sativa* L.), known as industrial hemp, is one of the world's oldest cultivated and most widely used industrial crops which has been cultivated for obtaining long and strong bast fibres. Hemp cultivation moreover allows a diversification of crop rotations in arable farming and has a low requirement for fertilizers and herbicides (Ranalli and Venturi 2004; Amaducci et al. 2014). The flowering top and to a lesser extent the leaves of hemp plants can produce resin secretions containing the narcotic 9-Δ tetrahydrocannabinol (THC), the psychoactive ingredient in marijuana and hashish (Shahzad 2011). However, industrial hemp varieties grown as plant fibre sources produce less than 0.3% dry weight of THC, which is too low to be directly used as a narcotic (Salentijn et al. 2015). The hemp bast fibres have long been used in textile production such as hemp garments and soft furnishings. The co-product, hemp seeds, is a source of more than 10 fatty acids which yield oil of up to 26 − 37% by weight (Da Porto et al. 2015).

Hemp bast fibres are defined as the continuum of primary and secondary cell walls of the cells that form the cortex sclerenchyma layer of the hemp stem. These bast fibres are particularly long and contain highly crystalline cellulose fibrils. These characteristics make hemp plants a promising source of natural cellulosic fibres (Liu et al. 2015a), including natural fibres for use in biocomposite materials. More importantly, compared to synthetic materials (e.g. glass fibre), hemp fibres also have other advantages such as low cost and low density together with their high stiffness- and strength- to-weight ratios (Faruk et al., 2012; Joshi et al., 2004; Liu et al., 2015; Reddy and Yang, 2008). However, their inherent disadvantages such as a hydrophilic surface, high moisture uptake and vulnerability to microbial attack challenge the direct application of the natural fibres as reinforcement in natural fibre reinforced composites (NFCs). Hydrophilic surfaces will cause weak bonding between fibres and matrix composite materials, particularly hydrophobic matrix polymers. Moisture uptake can thus induce dimensional changes (or swelling), decrease mechanical performance and confer higher susceptibility to microbiological attack. Targeted fibre pre-treatment is therefore important for tuning the properties of the natural fibres for optimal inclusion, mechanical performance, and durability for successful application in NFCs.

2. Natural fibre reinforced composites (NFCs)

A composite is considered to be any multiphase material that exhibits a significant proportion of the properties of the constituent phases in such way that a better combination of properties is realized (Callister, 1994). Many composite materials are composed of two phases: a continuous phase (the matrix) which surrounds the dispersed or discontinuous second phase (the reinforcement). In natural fibre reinforced composites (NFCs) natural plant fibres constitute the reinformement phase, whereas the matrix can be any (synthetic) polymeric material. In principle, the mechanical properties of a composite material thus depend not only on the fibres, but also on the degree to which an applied load is transmitted to the fibres by the matrix polymers under stress, and thus obviously vary depending on the nature of the matrix material as well (Callister 1994). **Figure 1** illustrates several important parameters that influence the mechanical properties of composites, i.e. NFCs. These factors include: (a) fibre properties; (b) matrix properties; (c) fibre length; (d) fibre packing ability; (e) fibre orientation; (f) porosity; (g) fibre volume content; (h) fibre/matrix interface properties (Pickering et al., 2015). Based on these parameters, there is a range of desired properties required to obtain unidirectional composites with high mechanical performance and long durability in practical use (Table 1), and there are both advantages and disadvantages of using natural plant fibres in NFCs (Table 2).

Natural fibres are mainly composed of cellulose and other non-cellulosic cell wall components, notably of hemicellulose and aromatic substances. These components provides opportunity to tailor and modify natural fibres with chemical agents and enzymes (Liu et al. 2016b; Liu et al. 2016c). Natural fibre treatments for NFCs are primarily targeted to remove non-cellulosic cell wall components to obtain well separated and cellulose rich fibres, but more recently, treatments are also designed to increase surface hydrophobicity, moisture resistance and microbiological decay resistance of fibres (Bessadok et al. 2007; Özmen 2012; Zhang and He 2013). A primary restriction for successful use of natural fibres in NFCs is the hydrophilic nature of the cellulose fibres, which, as already mentioned briefly above, may result in moisture sensitivity and low microbiological decay resistance of NFCs (Summerscales et al. 2010a) (Table 2). The hydrophobic nature of cellulose fibres, on the other hand, provides the possibility for chemical and enzymatic modification of the hydroxyl groups on fibre surfaces Generally, the purpose of targeted fibre treatment is to overcome the disadvantages of NFCs to obtain: (a) improved bonding between natural fibres and matrix polymers; (b) reduced moisture uptake/increased moisture resistance; (c) improved mechanical properties of natural fibres or avoidance of severe decrease in mechanical properties of natural fibres; (d) improved other properties of natural fibres or NFCs (e.g. thermal stability; anti-microbial degradation etc.) and thus in general combat the potential disadvantages of natural fibres versus synthetic fibers for use in NFCs (Table 2).

3. Plant fibre selection

3.1. Hemp fibres

Plant fibres, the most widely used natural fibres in composites, can be classified into four categories according to their tissue origin in the plant, i.e. whether they come from 1) seed hair, examples are cotton and kapok; 2) leaves or fruit envelopes, as e.g. sisal and coconut; 3) the stem (or bast), e.g. as is the case for fibres from hemp, flax and ramie; or from the 4) root, where examples include sugar beet and carrot (**Figure 2**) (Vaca-Garcia 2008; Summerscales and Grove 2014). According to current advances in NFCs, the majority of plant fibres currently considered as possible reinforcements for NFCs are bast fibres (Summerscales et al. 2010b; Mehmood and Madsen 2012; Pickering et al. 2015; Liu et al. 2016b; Liu et al. 2016c). One reason for this could be that bast fibres, notably bast fibres from hemp and flax, exhibit higher mechanical performances, e.g. strength of 400 – 1000 MPa and stiffness of 25−35 GPa, than fibres from other plant sources and categories, e.g. for cotton the strength is 290 – 600 MPa and stiffness is 5 – 13 GPa (Cierpucha et al. 2004; Vaca-Garcia 2008; Pil et al. 2016). Among commonly used bast fibres for NFCs, hemp bast fibres seem to be the most advantageous also because a) hemp is an extremely fast growing crop, yielding more fibres per acre than other crops such as kenaf (Herer 1985) and flax (van der Werf and Turunen 2008); b) hemp suppresses weeds effectively and is usually free from diseases or pests (van der Werf et al. 1996), and thus c) leave the soil in excellent condition for the succeeding crops, especially when weeds may be troublesome, whereas (non-organic) flax requires high agro-chemical inputs.

3.2. Hemp fibre structure

(1) At bast fibre level

Hemp stems are usually 1.5 – 2.5 m tall and 5 – 15 mm in diameter. The stem contains 30 – 40% (w/w) bast fibres and is organized in layers comprising from the pith to the surface 1 – 5 mm xylem, 10 – 50 µm cambium, 100 – 300 µm cortex, 20 – 100 µm epidermis and 2 −5 µm cuticle (Liu et al. 2015a) (**Figure 3**). Hemp bast fibres contain primary and secondary fibres situated in the cortex. The primary fibres are more suitable for NFCs because secondary fibres are shorter (approx. 2 mm long) and thinner (approx. 15 µm in diameter) than primary fibres (approx. 20 mm long and 10 – 40 µm in diameter) (van der Werf et al. 1994).

(2) At single fibre level

Similar to other plant fibres, hemp fibre cell walls are mainly composed of a thin primary wall (70 – 110 nm) and a thick secondary cell wall (3 – 13 µm) (Thygesen et al. 2006). The secondary cell wall is composed of a S1 layer (100 –

130 nm in thickness) and a S2 layer (3 – 13 µm in thickness) (Thygesen et al. 2006). The thicker S2 layer has been observed to have a laminate structure consisting of 1 – 4 major concentric layers with a thickness of 1 – 5 µm (**Figure 4**) (Thygesen et al. 2006). The construction varies greatly between the layers:

- the primary wall has loosely packed microfibrils which interweave randomly;
- the secondary walls have microfibrils closely packed and parallel to each other (Thygesen et al. 2006; Fan et al. 2011). Using X-ray diffraction, the cellulose microfibrils in the S1 layer have an S-helical orientation with microfibril angles (MFA) in the range of 70 – 90°, while in the S2 layer, the microfibrils have Z-helical orientation with MFA in the range of 25 – 30° (outer part) and 0 − 2° (inner part) (Thygesen et al. 2006).

(3) At microfibril level

The fibre cell wall can in itself be considered as a composite (**Figure 4**) composed of cellulose microfibrils as reinforcements and non-cellulosic polymers, mainly including hemicellulose, pectin, lignin, as matrix polymers (Lefeuvre et al. 2014). Cellulose microfibrils are cross-linked by glycans (e.g. xyloglucan, glucuronoarabinoxylan, galactomannan, mannan) (Carpita and Gibeaut 1993; Peña et al. 2008). The interlocked network of microfibrils and glycans is further embedded in a matrix of pectic substances and reinforced with structural aromatic substances (e.g. lignin and hydroxycinnamates) (Markwalder and Neukom 1976; Chesson et al. 1983; Carpita and Gibeaut 1993). The aromatic substances presumably add mechanical properties to the cell by interacting with polysaccharides via cross-linking reactions (Ralph 2010; Lupoi et al. 2015) and are associated with ageing and stiffening of the plant.

3.3. Chemical composition

Hemp fibres, similarly to other plant fibres, essentially contain 5 major components (Crônier et al. 2005; Liu et al. 2015a; Liu et al. 2015b): (1) structural polysaccharides: cellulose and hemicellulose (the hemicellulose mainly being xyloglucan); (2) structural protein; (3) other polysaccharides, notably pectin (homogalacturonan); (4) lignin; (5) waxes, and (6) minerals. Hemp fibres are generally composed of 53-91% cellulose, 4-18% hemicellulose, 1-17% pectin, and 1-21% lignin (**Table 3**) , but the chemical composition of untreated hemp bast fibres varies with the cultivar (see **Table 3**), harvest year (Jankauskiene et al. 2015), harvest time (or growing stage) (Crônier et al. 2005), the location of fibres within the stems (Charlet et al. 2007), and the final composition also depends on the type of fibre processing (Korte and Staiger 2008; Nykter et al. 2008). The chemical composition of fibres and the distribution of the constituents define the properties of the fibres (Komuraiah et al. 2014). Changes in chemical composition of natural fibres after different fibre processing regimes have been commonly used to explain changes in the mechanical properties of fibres and fibre/matrix polymers composites (Charlet et al. 2007; Thuault et al. 2013; Behazin et al. 2016).

3.4. Mechanical properties

The density of hemp fibres is 1.4-1.6 g/cm^3, whereas the mechanical properties of fibres from different hemp varieties, i.e. tensile strength, stiffness and failure strain range from 200-1000 MPa, 18-66 GPa, and 2-4%, respectively (**Table 4**). In comparison, synthetic fibres including glass fibres and carbon fibres have relatively high tensile strengths of ~2000 and up to ~4000 MPa, respectively, as well as higher average stiffness of 80 and 238 GPa, respectively (Table 4). Glass fibers have much higher density (2.55 g/cm^3) than hemp fibers, however, but carbon fibres have low density (1.3 g/cm^3) (**Table 4**). Thus, the *specific* tensile strength (1.3- 6.7 × 10^5 m^2/s^2) and stiffness (1.2-4.4 × 10^7 m^2/s^2) of hemp fibres are comparable to the specific tensile strength (approx. 7.6 × 10^5 m^2/s^2) and stiffness (approx. 3.0 × 10^7 m^2/s^2) of glass fibres. Hemp fibres therefore have potential as replacements for glass fibre as reinforcements for composite materials.

However, as evident when comparing the available data for hemp fibres (**Table 4**) there is large variability in the mechanical properties of hemp fibres. Many efforts have been made to understand the properties determining the mechanical properties of hemp fibres (Charlet et al. 2007; Marrot et al. 2013). A number of studies indicate that many inherent factors may affect the mechanical properties of natural fibres, including notably the chemical composition (Charlet et al. 2007; Bourmaud et al. 2013; Marrot et al. 2013), microfibril angle (Baley 2002; Neagu 2005; Nilsson and Gustafsson 2007; Dai 2010; Bourmaud et al. 2013), structure of fibre cell walls (Carpita and Gibeaut 1993; Álvarez et al. 2011; Marrot et al. 2013), in addition to damage incurred during growth and processing. Even for untreated hemp fibres, there is a large scatter in their mechanical properties. In addition to the factors that affect the chemical composition, the factors affecting the mechanical properties of untreated hemp bast fibres include variety (Marrot et al. 2013), growth stage of the plant at harvest (Keller et al. 2001; Liu et al. 2015a), growth conditions (van der Werf et al. 1995), stem section (Duval et al. 2011; Liu et al. 2015b).

Marrot et al. (2013) compared the mechanical properties of hemp fibres from two different varieties of hemp plants, i.e. Fedora 17 and Felina 32 and found that the two types of fibres exhibited different tensile strength, stiffness and strain, which was attributed to the differences in chemical composition especially matrix polymers e.g. pectin between the two types of investigated fibres. Similar results were reported for flax fibres (Bourmaud et al. 2013). The growth stage of the hemp plant has also been found to influence the mechanical properties of the fibres (Keller et al. 2001; Liu et al. 2015a). Fibres from hemp plants harvested at the beginning of flowering thus had higher tensile strength (i.e. 950 MPa) and stiffness (i.e. 35GPa) than fibres from hemp plant harvested at seed maturity with a tensile strength of 810 MPa and stiffness of 31 GPa (Liu et al. 2015a). The low mechanical performance of fibres from hemp plants harvested

at seed maturity are suggested to be mainly due to low cellulose and partly low pectin content and to formation of secondary fibres which are shorter and have less favorable mechanical properties than primary fibres (Liu et al. 2015a).

Apart from the factors mentioned above, the location of the fibres in hemp stems also influences the mechanical properties of the hemp fibres (Duval et al. 2011; Liu et al. 2015b). Hence, fibres from the middle section of the hemp stem had highest mechanical properties followed by fibres from the top and bottom sections. The differences in mechanical properties of hemp fibres from different stem sections are attributed to the differences in their chemical composition particularly the cellulose and pectin content, and to the proportion of secondary fibres (Liu et al. 2015b).

4. Matrix polymer

For a fibre reinforced polymer composite, stiffness and strength of the matrix polymer are lower than that of the reinforcements. Matrix polymer, an important part of the NFCs, protects reinforcements against adverse environments, mechanical abrasion, and transfers stresses to the different forms of reinforcements (e.g. fibres or fibre fabrics) in different shapes to meet practical needs (Pickering et al. 2015). Natural fibres are sensitive to water and high temperature. Therefore, the most commonly used matrix polymers in NFCs are those that can be processed (i.e. melted or cured) at low temperature (e.g. below 200 °C) and which have low water content. Those polymers can be categorized as thermoset and thermoplastic polymers, respectively.

A large range of thermoplastic polymers (Table 5) and thermoset polymers (Table 6) have been applied for NFCs. These polymers commonly have a density of 0.9 – 1.6 g/cm^3, and stiffness of 0.2 – 14 GPa. As mentioned, the melting point as well as the curing temperature of commonly used thermoplastic and thermoset polymers is below 200 °C. In practice, this relatively low temperature required for the processing, means that manufacturing of NFCs with such polymers does not significantly influence the mechanical properties of the resultant NFCs. However, the glass transition temperature (T_g) is normally 200 ± 50 °C below the crystalline melting point (T_m), so a thermoplastic matrix system that can be processed without degrading the fibres is unlikely to be useable when creep deformation may occur. Exceptions include poly (lactic acid) (PLA) or thermosetting resins where the T_g is close to the maximum cure temperature.

5. Pre-treatment of hemp fibres affecting mechanical performance of NFCs

As already stressed in Section 2, above, the hydrophilic character of natural fibres is generally considered a major barrier for use of natural fibres in composites where high reliability and stability of fibre properties are required. The hydrophilic character of natural fibres can cause the following issues in NFCs: 1) Decreased interfacial contact between the natural fibre and the matrix polymer; 2) water uptake which in turn may decrease stability and durability of the

NFCs, and 3) provide conditions for microorganisms to thrive. The pretreatment or processing of the natural fibres may however be designed to help alleviate the hydrophilicity and even provide for enhancing the natural properties of the fibres for successful use in NFCs. It is however important to understand the effects of fibre pre-treatments on the mechanical properties of NFCs in order to provide optimal cost-benefit fibre treatments.

5.1. Defibration

The defibration process, a term commonly used for the pulping processes for paper, involves breakdown of the wood matrix and results in separation of the fibres. In relation to fibre processing for use in NFCs, the defibration process refers to the treatments applied to degrade non-cellulosic components of the natural fibres to produce small fibre bundles (technical fibres) or single fibres (ultimate fibres) from large fibre bundles. Several fibre treatment methods, including traditional retting, steam explosion, chemical treatment, controlled fungal retting and enzyme treatment etc., have been tested to defibrate natural fibres for composites use. Optimal defibration of natural fibres produces increased surface area for contacting with matrix polymers and allow for the matrix polymers to fill the space between fibres or fibre bundles (Liu et al. 2016b). Interfacial contact, i.e. the bonding or attachment, between the fibres and the matrix polymer is therefore increased. Furthermore, defibration of natural fibres produces cellulose-rich fibres by removal of non-fibre cells that have large voids (i.e. parenchymal and epidermal cells), and this may in turn decrease the porosity of the resultant composites. Consequently, the mechanical properties of NFCs can be increased by correct defibration.

5.1.1. Traditional retting

Retting is a process resting on the (random) action of microorganisms to remove non-cellulosic components from natural fibres and separate fibres from the plant stem structure so as to obtain cellulose-rich fibres (Thygesen et al. 2013). Two retting methods have been traditionally used: field retting (also known as dew retting), and water retting.

In field retting, plant stems are cut and spread out in the fields where they are casually attacked by microbial activities (Liu et al. 2015a). The growth of microbial communities, especially the pectinolytic microbial communities, largely depends on the local microbiota, the moisture content of plant stems, and on the humidity and temperature under local weather conditions. Therefore field retting is subject to geographical variation and depend on whether the weather conditions are suitable for microbial proliferation; the retting processing usually takes several weeks (Jankauskienė and Gruzdevienė 2013; Liu et al. 2015a). Water retting is performed by submerging plant stems in water in rivers, lakes or tanks where pectinolytic microbial communities develop. The water can penetrate into the plant stem structures, increase the moisture absorption of plant samples, and boost the proliferation of microorganisms. Usually, water retting takes less time e.g. 1-2 weeks than field retting (Thygesen et al. 2013; Jankauskienė and Gruzdevienė 2013).

We have studied the effect of field retting on chemical composition and mechanical properties of hemp fibres and hemp fibre/epoxy composites (Liu et al. 2015a; Liu et al. 2016d) and found that both fungal and bacterial communities were involved in field retting. Species of the Ascomycota phylum were observed during the first 1 – 2 weeks of field retting, after which different types of bacteria, notably different Proteobacteria proliferated during the 2nd to the 3rd week of retting (Liu et al. 2016d). Different enzyme activities were observed in field retted samples including glucanase, polygalacturonase, galactanase, and xyloglucan (XG)-specific endoglucanase (Liu et al. 2016d). A summary of the enzyme activities recorded during field retting are shown in Table 7.

In field retting, pectin as assessed by galacturonic acid (polygalacturonan) content is gradually removed during the retting in response to the presence of pectinolytic enzyme activities. The polygalacturonan content of hemp fibres was thus found to decrease to 3 – 4% from 8% after 2 weeks of field retting (Liu et al. 2015a; Liu et al. 2016d). However, the cellulose content of hemp fibres also decreased during field retting, particularly after 2 weeks (Liu et al. 2015a), in accord with the presence of glucanase activity in the field retted samples (Liu et al. 2016d). The stiffness of hemp fibres decreased from 31 GPa to 28 GPa and tensile strength decreased from 810 MPa to 680 MPa after 20 days of field retting (Liu et al. 2015a). This decrease in mechanical properties of fibres was attributed to the loss and damage of the cellulose in the fibres (Liu et al. 2015a).

When the effect of field retting and water retting on chemical composition and physical properties of hemp fibres was compared it has been found that water retted hemp fibres had higher content of cellulose (81.7%), hemicellulose (6.3%) and lower content of lignin (10.2%) when compared with that of field retted fibres (78.4%, 5.9% and 13.1%, respectively) (Jankauskienė and Gruzdevienė 2013). Candilo et al. (2010) compared the performance of a traditional water retting process, without inoculum, and a modified water retting process inoculated with two selected pectinolytic bacteria (i.e. an anaerobic strain *Clostridium* sp. L1/6 and an aerobic strain *Bacillus* sp. ROO40b) for hemp fibre treatments and fouond that the modified water retting process speeded up the retting process and significantly improved fibre quality (Di Candilo et al. 2010). The best fibre quality with a cellulose content of 89% could be obtained after only 3 – 4 days of retting with the addition of the bacterial inoculum (Di Candilo et al. 2010). Thygesen et al. (2013) compared the morphology of cross sections of composites made with water retted hemp fibres and untreated fibres and found that water retting appeared to improve the interface between fibres and polymer matrix (i.e. epoxy) and that water retted fibres reinforced epoxy composites had fewer voids than the benchmark (Thygesen et al. 2013). Generally, it is thus believed that water retting provides higher retting efficiency and stronger fibres than field retting.

Undoubtedly, traditional water retting of hemp consumes large amounts of freshwater, and causes eutrophication (van der Werf and Turunen 2008). Efforts have been made to make this treatment less reliant on the availability of water resources by using seawater to substitute fresh water for water retting (Zhang et al. 2008). It was found that seawater works as well as fresh water in retting of hemp fibres with regard to the removal of non-cellulosic components, as pectin content decreased from 6.5% to 0.4% after 2 weeks of seawater retting (Zhang et al. 2008).

5.1.2. Steam explosion

Steam explosion is a thermo-mechanical-chemical defibration method which allows breakdown of the lignocellulosic structural components via a sharp pressure change. Steam explosion has been widely used as a pre-treatment technology for lignocellulosic materials to improve enzyme catalyzed cellulose degradation (Jacquet et al. 2015), and has also been used for pre-treatment of natural fibres intended for use in composites in order to defibrate fibre bundles into single fibres and small fibre bundles by degrading or disrupting the middle lamella (ML) between the individual fibres (Vignon et al. 1996; Keller 2003; Thomsen et al. 2006; Kukle et al. 2011).

Keller (Keller 2003) compared biological processes and steam explosion for pectin degradation on hemp fibres, and studied the mechanical performance of the treated fibres in composites. Hemp fibres produced from steam explosion were four times as long (~ 0.10 mm) as the fibres obtained after biological treatment and steam exploded fibres therefore had a significantly higher aspect ratio (i.e. 23) than biologically treated hemp fibres (i.e. 4). Composites with a fibre volume fraction of up to 42% of steam exploded hemp fibres having a tensile strength of up to 30 MPa and stiffness of up to 4 GPa could be achieved. Steam explosion was also shown to be more effective in degrading pectin from the middle lamella regions, allowing production of small fibre bundles and elementary bast fibres, when steam explosion treatment was combined with biological retting pre-treatment (Vignon et al. 1996). A similar conclusion was drawn from results showing that steam explosion of retted hemp fibres increased the cellulose content of the fibres from 73% to 85 – 90%, while that of raw hemp fibres was increased from 60 – 64% to 73 – 75% (Thygesen 2006). Further confirmation was made that combination of retting methods and steam explosion gave good disintegration of hemp fibres, and that alkali pre-treatment after retting is not necessary prior to steam explosion (Kukle et al. 2011).

5.1.3. Chemical treatment

Chemical treatment involves use of different chemicals to remove non-cellulosic components, i.e. particularly pectin, hemicellulose and lignin, from natural fibres. Chemical chelators such as ethylenediaminetetraacetic acid (EDTA) and ethylene diamine tetra (methylene phosphonic acid) (EDTMPA) have been applied in natural fibre defibration to loosen the structure of pectin (Evans et al. 2002; Stuart et al. 2006; Thygesen et al. 2006; Li and Pickering 2008; Bacci et al.

289 2010; Liu et al. 2016b). Alkalis such as sodium hydroxide (NaOH) and potassium hydroxide (KOH) are commonly
290 used to help remove hemicellulose (e.g. xyloglucan) from natural fibres. Other non-cellulosic components, notably
291 lignin and pectin can also be partially removed by alkali treatments (Korte and Staiger 2008; Sawpan et al. 2011a; Liu
292 et al. 2016b). Sodium sulphite (Na_2SO_3) is also commonly used together with alkali to remove lignin (Wang et al.
293 2003).

294 Pectin is mainly located in the middle lamella (ML) of hemp fibres where it functions as glue packing the single
295 fibres together. Removal of pectin improves production of small cellulosic fibre bundles or individual fibres. The most
296 abundant pectic polysaccharide in plant cell walls is homogalacturonan (HG). Calcium, as described by the ″egg-box"
297 model, is important for stabilizing the structure of HG via calcium-mediated interactions (Liners et al. 1989). Chemical
298 chelators such as EDTA and EDTMPA are capable of removing calcium from natural fibres through competitive
299 chelation of calcium (Griko 1999).

300 We have recently studied the effect of different concentrations of EDTA on the removal of calcium and HG from
301 hemp bast fibres (Liu et al. 2016b). Calcium removal from hemp fibres was shown to be positively correlated with the
302 concentration of EDTA used. The calcium released increased from 6 (mg/100 g dry matter) in the control treatment (i.e.
303 0% EDTA) to 490 (mg/100 dry matter) with 0.5% EDTA treatment, and finally to about 800 (mg/100g dry matter) with
304 treatment with 2% or 3% EDTA, respectively (Liu et al. 2016b). The removal of HG from hemp fibres correlated
305 positively and linearly with calcium removal by EDTA with a slope of 1.0 (mole ratio of galacturonic acid and calcium
306 release) (Liu et al. 2016b). With the removal of calcium, more HG was thus removed from hemp bast fibres. After
307 EDTA treatment, slightly increased separation of hemp fibres has been observed in several studies (Le Troedec et al.
308 2008; Li and Pickering 2008; Liu et al. 2016b) and improved mechanical properties of hemp fibre reinforced polymer
309 composites made from EDTA treated hemp fibres have been reported (Li and Pickering 2008). In our own work, we
310 obtained composites with lower porosity and higher mechanical properties with EDTA treated fibres compared to
311 composites made with untreated fibres (Liu et al. 2016b). However, the data have also revealed that pectin can only be
312 partially removed by EDTA treatment, even though most of the calcium in hemp fibres can be removed (Liu et al.
313 2016b). Enhanced pectin removal was achieved by combining chemical chelators and pectinolytic enzymes (i.e.
314 polygalacturonase treatment) (Li and Pickering 2008; Liu et al. 2016b). The combined treatment with chemical
315 chelators and enzymes will be discussed in detail in sections 5.1.4 and 5.1.5.

316 Alkali extraction with NaOH or KOH is widely used for the isolation of hemicellulose from lignocellulosic biomass
317 to obtain cellulose of high purity (Puls et al. 2006). We have previously investigated the effect of removal of

hemicellulose with 10% NaOH after pectin was removed by EDTA and pectinase and found that up to 70% of the hemicellulose could be removed from hemp fibres by NaOH (Liu et al. 2016b). This removal of pectin and hemicellulose promoted separation of the hemp fibres and improved the cleanliness of the fibre surface (Liu et al. 2016b), as shown in **Figure 5**. These changes in fibre morphology and degree of fibre separation resulted in significantly increased stiffness of the resultant composites; the improved stiffness was interpreted to be mainly due to the increased cellulose content of the fibres (up to 86%) as well as decreased composite porosity as a result of the improved interface bonding between the fibres and the matrix polymers, as confirmed by ESEM micrographs (Liu et al. 2016b). However, the tensile strength of composites with NaOH treated fibres decreased, apparently as a result of disruption of the cellulose-hemicellulose interlocked network after NaOH treatment (Liu et al. 2016b).

Treatments combining alkali and sodium sulphite have also been shown to be effective in lignin removal from hemp fibres, and the concentration levels of both NaOH and Na_2SO_3 are known to significantly affect lignin removal (Wang et al. 2003). Combined treatment with alkali (i.e. 5% NaOH) and sodium sulphite (i.e. 2% Na_2SO_3) was reported to enhance separation of fibres from fibre bundles, remove lignin and the other components, expose cellulose hydroxyl groups, make the fibre surfaces cleaner and also enhance thermal stability of the fibres by increasing cellulose crystallinity in turn improving the mechanical properties of hemp fibre/epoxy composites (Islam et al. 2011).

5.1.4. Controlled microbiological retting

Controlled microbiological retting is a process employing controlled incubation of stems or bast fibres with selected microorganisms, which secrete enzymes (notably pectinolytic enzymes) that attack the non-cellulosic components of natural fibres during the retting incubation. Traditional field retting and water retting are not well controlled and depend on both spontaneous proliferation of microbes prevalent in the particular geographic region and on the availability of water, i.e. via atmospheric precipitation. Controlled microbiological retting can overcome some of the disadvantages of traditional retting methods and also greatly speed up the retting process.

Thygesen et al. compared the mechanical properties of composites made from controlled fungally defibrated hemp fibres with composites made from traditional water retted hemp fibres (Thygesen et al. 2007). Two strains of white rot fungi, *Phlebia radiata* Cel 26 (a mutated fungus low in cellulase expression) and *Ceriporiopsis subvermispora*, were employed in the controlled microbiological (fungal) treatment. Fibres produced via controlled retting with *P. radiata* Cel 26 had higher cellulose content (78%, w/w) than water retted hemp fibres (74%) and *C. subvermispora* retted fibres (72%). Hemp fibres retted with *P. radiata* Cel 26 moreover exhibited the highest effective stiffness and strength in composites (94 GPa and 643 MPa, respectively) compared to water retted fibres (88 GPa and 586 MPa, respectively).

The improvement in the mechanical performance of epoxy composites reinforced with *P. radiata* Cel 26 retted fibres was explained as being due to improved surface contact between the hemp fibres and the epoxy polymer matrix (Thygesen et al. 2007).

In further studies of retting of hemp stems from different stem sections (i.e. top, middle and bottom) with *P. radiata* Cel 26 and *C. subvermispora*, respectively, it was also found that *P. radiata* Cel 26 exhibited higher depectinization selectivity and efficiency than *C. subvermispora* (Thygesen et al. 2013; Liu et al. 2015b). Moreover, fibres retted with *P. radiata* Cel 26 had better mechanical properties with tensile strength, strain and stiffness of 736 MPa, 2.3% and 42 GPa than the fibres treated with *C. subvermispora*. In a more thorough comparison between fungal retting of hemp fibres with *P. radiata* Cel 26 and traditional field retting, including examination of differences in enzyme activities and mechanical properties of fibres and fibre reinforced composites resulting from the treatments, a lower β-glucanase activity and higher polygalacturonase activity was demonstrated in *P. radiata* Cel 26 retted hemp fibres than in field retted samples (Table 6) (Liu et al. 2016d). Composites made with *P. radiata* Cel 26 retted hemp fibres exhibited significantly higher strength and stiffness than composites made with field retted fibres (Liu et al. 2016d).

Li et al. compared the mechanical properties of hemp fibres and their composites after 2 weeks of fungal retting with the white rot fungi *Schizophyllum commune* (Li et al. 2009). Composites with fibres treated with *S. commune* had a higher tensile strength of 45 MPa and stiffness of 7 GPa compared to the composites with untreated fibres which had tensile strength of 35 MPa and stiffness of 4 GPa (Li et al. 2009). Results from both single fibre pull-out tests and the Bowyer and Bader model (Li et al. 2009) moreover showed that the interfacial shear strength (IFSS) of *S. commune* treated fibre composites was higher than that of untreated fibre composites. Based on these data it was suggested that the hemp fibre interfacial bonding with polypropylene matrix was improved by white rot fungi treatment with *C. commune*. In general, the findings reported by Li et al. are consistent with the studies by Thygesen et al. (Thygesen et al. 2007; Thygesen et al. 2013) and Liu et al. (Liu et al. 2016d).

5.1.5. Enzyme treatment

Enzymes, as biocatalysts, can catalyze selective removal of non-cellulosic components from hemp fibres. Compared to chemical treatment, biocatalyzed reactions can be performed under mild conditions, i.e. low temperature and near neutral pH. Enzyme treatment involving mainly pectinolytic enzymes thus offers an environmentally friendly as well as an efficient method for separating fibres and removing non-cellulosic components from natural plant fibres. In practice, treatment of natural plant bast fibres with pectinolytic enzymes (e.g. endo-polygalacturonase) induce release of pectic polymers from the ML and fibre cell walls as the enzymes catalyze random hydrolysis of the glycosidic bonds of the

HG backbone to liberate monomeric, dimeric or oligomeric fragments (Benen et al. 1999). After removal of pectin from the ML, the bonding between fibres becomes weaker and individual fibres and small fibre bundles can be separated from the larger fibre bundles (Liu et al. 2016b).

We recently employed 0.2% of a mono-active fungally derived endo-polygalacturonase to treat hemp fibres to investigate the effect of the treatment on fibre and fibre reinforced composite properties (Liu et al. 2016b). After endo-polygalacturonase treatment, the polygalacturonan content decreased to 4.8% from 8.3% in untreated hemp fibres (Liu et al. 2016b). The fibre surfaces became cleaner after the treatment and improved mechanical properties of fibre reinforced composites were obtained compared to the composites produced with traditional field retted fibres (Liu et al. 2016b). The pectin removal results were in accord with those of (Li and Pickering 2008) who reported a decrease in pectin content from 6.2% in untreated fibres to 5.7% after hemp fibres were treated with pectinase. However, the enzymes cannot directly penetrate the hemp fibres to degrade pectins efficiently. The accessibility of the substrate surface to enzymes is therefore important in enzyme treatment of natural fibres, and pre-treatment of natural fibres is thus necessary to achieve well separated fibres with pectinase treatment.

As mentioned above, addition of chemical chelators (e.g. EDTA) has been shown to promote enzyme catalyzed degradation of HG from cellulosic fibres during pectinase treatment (Adamsen et al. 2002; Stuart et al. 2006). As mentioned, the enhanced enzymatic degradation of HG results from the capacity of chemical chelators to competitively form complexes with divalent ions, in turn removing e.g. calcium from pectin (Griko 1999). We found that once 0.5% EDTA was added to 0.2% endo-polygalacturonase during hemp fibre treatment, a significantly higher amount of pectin was removed, leaving only 2% polygalacturonan left in the fibres, compared to 5% for fibres treated with enzyme alone (Liu et al. 2016b). This enhanced pectin removal produced better separation of hemp fibres from fibre bundles and also improved the mechanical properties of the hemp fibre/epoxy composites (Liu et al. 2016b). Enhanced enzymatic removal of pectin and improved mechanical properties of fibre reinforced composites after hemp fibres were treated with chemical chelators and pectinases have also been reported in other studies (Li and Pickering 2008).

Besides use of chemical chelators, hydrothermal pre-treatment was found to improve enzymatic removal of pectin from hemp fibres (Liu et al. 2016c). A systematic investigation of hydrothermal pre-treatment at different severities (i.e. 30 min at 112 °C, 121 °C and 134 °C, respectively) to promote enzymatic treatment of hemp fibres with pectinases showed that mild hydrothermal pre-treatment could impart better enzymatic removal of pectin from the hemp fibres to produce cellulose rich fibres without damaging the fibre properties (Liu et al. 2016c). It was also found that hydrothermal pre-treatment at 121 °C for 30 min followed by a 90 min pectinolytic enzyme treatment resulted in hemp

fibres with low pectin content of 3%, high tensile strength of 780 MPa and stiffness of 36 GPa; fibres treated using this method could be used to make fibre/epoxy composites with tensile strength of 325 MPa and stiffness of 38 GPa at a fibre volume content of 50% (Liu et al. 2016c).

5.1.6. Correlation between fibre defibration and mechanical properties NFCs

As summarized above, increased tensile strength and stiffness of NFCs have been observed after fibres were pre-treated using different fibre pre-treatment methods. Fibre pre-treatment primarily affects chemical composition of fibres by removing non-cellulosic components (e.g. pectin and hemicellulose), and produces well separated fibres. Good separation of fibres in turn improves interfacial bonding between fibres and matrix polymers. As a result, increased tensile strength and stiffness of NFCs are achieved. Recently, the correlation between different fibre pre-treatment methods and mechanical performance of NFCs with differently treated hemp fibres was established by Liu et al. (2016b). The correlation was established between chemical composition of hemp fibres and porosity (as indicated by fibre correlated porosity factor) of hemp fibre reinforced composites (Liu et al. 2016b), as shown in **Figure 6**. It was found that less pectin and hemicellulose content of fibres after different treatments resulted in lower porosity of NFCs (Figure 6a). The decrease in porosity of NFCs was explained by changes in fibre microstructure (e.g. fibre separation) and cleanliness of fibre surface after fibre treatment (Liu et al. 2016b). Consequently, increased tensile strength and stiffness of NFCs were obtained via decreasing the porosity of NFCs: The lower the NFC porosity is, the higher is the mechanical performance (Figure 6b) (Liu et al. 2016b). Traditional field retting does not fit such correlation (Figure 6), which may be due to degradation of cellulose caused by field retting (Liu et al. 2016b).

5.2. Polymerization/Cross-linking

Natural fibres can be considered as a composites with cellulose reinforcement in non-cellulosic (i.e. pectin and lignin) matrix polymers. Pectin and lignin are mainly located in the ML regions between fibres. Lignin in hemp fibres accounts for 2 – 5% of dry matter of the fibre cell walls. Previous studies have shown that model lignin compounds can be catalyzed by laccases or peroxidases to form complex structures, and laccases can also catalyze polymerization of different types of lignin to different degrees (Ikeda et al. 1996; Mattinen et al. 2008). The polymerization of lignin and other aromatic substances has been suggested to improve the mechanical properties of plant cell walls (Ralph 2010).

We recently studied the effect of laccase treatment of hemp fibres on properties of fibres and their composites (Liu et al. 2016a). After the hemp fibres were pre-treated with 0.5% EDTA and 0.2% endo-polygalacturonase (EPG), laccase treatment was found to increase stiffness of the resulting fibres and unidirectional hemp fibre/epoxy composites. The resultant composites had stiffness of up to 42 GPa and tensile strength of up to 326 MPa at a fibre volume content of

50% (Liu et al. 2016a). The thermal resistance of hemp fibres also increased after laccase treatments, and the maximum degradation temperature increased by about 5 °C. These changes in the mechanical properties of hemp fibres and their composites were attributed to polymerization of lignin by laccase (Liu et al. 2016a).

Improvement in the mechanical properties of natural fibres after laccase treatments was also observed for plantain fibres (Álvarez et al. 2011). An increase in the maximum degradation temperature and mechanical properties of treated fibres with increasing concentration of laccase used in the treatment was observed (Álvarez et al. 2011). The maximum degradation temperature increased from 327 °C for the control to 328 °C for fibres treated with laccase at a concentration of 6 U/g dry matter, to 329 °C for fibres treated with laccase at a concentration of 12 U/g dry matter, and finally to 331 °C for fibres treated with laccase at a concentration of 24 U/g dry matter; for the same series of laccase concentration treatments, stiffness of the resulting fibres increased from 1.3 GPa, to 3.5 GPa, to 3.6 GPa, and finally to 3.6 GPa, respectively and tensile strength increased from 13.3 MPa, to 17.5 MPa, to 18.6 MPa, and finally to 18.7 MPa, respectively (Álvarez et al. 2011).

5.3. Surface modification

The hydrophilic nature of cellulose rich fibres is a restriction for successful use of natural fibres in composite applications. The hydrophilicity of natural fibres is mainly contributed by hydroxyl groups of cellulose and other hydrophilic non-cellulosic components. Surface modification aims to reduce the hydrophilic nature of cellulose rich fibres mainly by replacing hydroxyl groups of cellulose with less hydrophilic (e.g. O^-Na^+) or hydrophobic chemical groups (e.g. acetyl groups (CH_3CO)). Reduction of the hydrophilic nature of cellulose rich fibres is thought to increase bonding between fibres and hydrophobic polymers. The increased bonding in turn improves the mechanical and physical properties of NFCs.

5.3.1. Alkali treatment

Besides the removal of a certain portion of hemicellulose and lignin, alkali (NaOH) treatment can reduce the amorphous hydroxyl group by the reaction between alkali and hydroxyl groups, as shown below. (Kabir et al. 2013). The removal of hemicellulose and lignin covering materials can expose more hydroxyl groups of cellulose to alkali. As a result, the hydrophilic nature of natural fibres is reduced and the surface of natural fibres become very clean and smooth (Sawpan et al. 2011a; Liu et al. 2016b), and those changes can improve adhesion between fibres and matrix binders. The effect of alkali treatment on fibre chemical composition, mechanical properties of fibres, and fibre reinforced composites has already been discussed in detail in Section 5.1.4.

$$\text{Fibre} - \text{OH} + \text{NaOH} \rightarrow \text{Fibre} - \text{O}^-\text{Na}^+ + \text{H}_2\text{O}$$

463 **5.3.2. Esterification**

464 Esterification treatment is commonly used to reduce the hydrophilic character of natural fibres by forming ester
465 bonds between hydroxyl groups of cellulose rich fibres and carboxylic acid groups of other chemical reagents such as
466 acetic anhydride, maleic anhydride, and vinyl acetate. The esterification reaction may be conducted at room temperature
467 or at elevated temperature with or without catalysts (e.g. acids, pyridine or potassium carbonate) (Özmen 2012; Kabir et
468 al. 2013). Acetylation is one of the most commonly used esterification reactions to replace hydroxyl groups (OH) with
469 the acetyl groups (CH_3CO) by using acetic anhydride (i.e. glacial acetic acid) or vinyl acetate as reagents.

470 Kabir et al. characterized the changes in chemical composition of hemp fibres after alkali (i.e. NaOH) pre-treatment
471 followed by acetyl treatment with glacial acetic acid at room temperature without catalysts (Kabir et al. 2013). Their
472 work confirmed that acetyl treatment with glacial acetic acid on hemp fibres can remove hemicellulose and lignin
473 constituents that cause increased thermal resistance (Kabir et al. 2013). Up to 6% ester content (g ester/ 100 g dry
474 matter of fibres) has been obtained after acetyl treatment of hemp fibres with acetic anhydride was performed for 120
475 min (Tserki et al. 2005). The removal of non-crystalline constituents of hemp fibres and slight decrease in fibre
476 crystallinity as a result of esterification were revealed using scanning electron microscopy (SEM) and X-ray diffraction
477 (XRD), respectively (Tserki et al. 2005).

478 Successful acetylation of hemp fibres with acetic anhydride in the presence of pyridine or potassium carbonate has
479 been achieved and this treatment resulted in a weight percentage gain (WPG) of 14% and 16%, respectively (Özmen
480 2012), whereas a WPG of 15% was achieved from acetyl treatment of hemp fibres with vinyl acetate in the presence of
481 potassium carbonate, but no weight gain (0% WPG) was obtained when pyridine was used as catalyst (Özmen 2012).
482 After hemp fibres were acetylated, the maximum weight loss temperature increased about 15 °C when compared with
483 untreated hemp fibres (Özmen 2012) .

484 The effect of surface treatment of hemp fibres using acetic anhydride and maleic anhydride on interfacial shear
485 strength (IFSS) of hemp fibre reinforced polylactide (PLA) and unsaturated polyester has also been investigated: The
486 IFFS of hemp fibre/PLA composites increased after acetic anhydride treatment. The increased IFFS from acetic
487 anhydride treatment was explained as being due to improved bonding between PLA and hemp fibres and increased PLA
488 transcrystallinity (Sawpan et al. 2011b). The IFSS of hemp fibre/unsaturated polyester also increased after both acetic
489 anhydride and maleic anhydride treatments, and the increased IFFS was interpreted to be due to improvement in
490 chemical bonding between the treated hemp fibres and the unsaturated polyester (Sawpan et al. 2011b).

491 **5.3.3. Graft co-polymerization**

492 Wettability of fibres by matrix polymers can be increased by graft copolymerizing short-chain molecules and
493 polymers onto the fibre surface using silane coupling agents or other copolymers or functional molecules such as
494 isocyanatoethyl methacrylate (IEM) (Chen et al. 2013), glycidyl methacrylate (GMA) (Moawia et al. 2016), methyl
495 methacrylate (MMA) (Singha and Rana 2010), or alkyl gallates (Ni et al. 2015).

496 Alkoxy silane is a multifunctional molecule which is commonly used as a coupling agent to modify natural fibre
497 surfaces (Alix et al. 2009; Sawpan et al. 2011a; Sawpan et al. 2011b; Kabir et al. 2013). Alkoxy silanes can form
498 chemical bonds with hydroxyl groups on fibre surfaces. During silane treatment, silanes undergo hydrolysis,
499 condensation and the bond formation stage. In the first step, silanols are formed after alkoxy silanes are hydrolyzed in
500 the presence of moisture (Sreekala et al. 2000). The silanols then react with the hydroxyl groups on fibre surface in the
501 condensation stage and eventually forms chemical bonds (i.e. fibre – O − Si).

502 Kabir et al. (Kabir et al. 2013) assessed the effect of silane treatment after alkali pre-treatment on chemical
503 composition and physical properties of hemp fibres and found that silane formed coverings on the fibre surfaces and
504 filled the spaces between the microfibrils without effects on chemical composition of hemp fibres (Kabir et al. 2013).
505 Sawpan et al. observed increased interfacial shear strength (IFSS)of hemp fibres reinforced polylactide (PLA) and
506 unsaturated polyester (UPE) composites after silane treatments (Sawpan et al. 2011b). The increased IFSS from silane
507 treatments was ascribed to improved compatibility between hemp fibres and matrix polymers. The highest IFSS of 20.3
508 MPa was obtained for the combined sodium hydroxide and silane treated hemp fibre/UPE composites (Sawpan et al.
509 2011b). Furthermore, slight decrease in average tensile strength of fibres from 577 MPa for untreated fibres to 554 MPa
510 for silane treated fibres was observed. The decrease in average tensile strength of fibres was explained by the decrease
511 in cellulose crystallinity after silane treatment (Sawpan et al. 2011a). However, the average stiffness of fibres increased
512 to 29.9 GPa after silane treatments, compared to 26.5 GPa for untreated fibres, and the increased stiffness was
513 presumably due to the removal of non-cellulosic components during silane treatments (Sawpan et al. 2011a).

514 After pre-treatment of hemp fibres with alkali, silane treatments have not led to apparent improvements in
515 mechanical and physical properties of hemp fibre reinforced composites (Kabir et al. 2013; Panaitescu et al. 2016). This
516 was probably because only amorphous hydroxyl groups can react with the functional groups of the coupling agents.
517 When hemp fibre is pre-treated with alkali, less hydroxyl groups are accessible to react with the functional groups of
518 silanes. Therefore other studies have been made on the effects of silane treatments on mechanical properties of hemp
519 fibres without alkali pre-treatment (Lu and Mysore Bhogaiah 2011; Panaitescu et al. 2016). These studies showed that

without alkali pre-treatment, treatment with 5% (w/w) triethoxyvinylsilane for 3 hours could increase the thermal stability of hemp fibres, and temperature at 50% weight loss of hemp fibres increased to 358 °C after silane treatment from 337 °C for untreated fibres (Lu and Mysore Bhogaiah 2011). A comparison has previously been conducted on the effect of silane treatments with three different silanes, (i: γ−aminopropyltriethoxysilane (APS), ii: γ−glycidoxypropyltrimethoxysilane (GPS), and iii: γ−methacryloxypropyltrimethoxy–silane (MPS)) without alkali pre-treatment on mechanical properties of hemp fibres/polypropylene (PP) composites (Panaitescu et al. 2016). The highest increase in composite stiffness was achieved when fibres were treated with MPS, followed by APS and then GPS (Panaitescu et al. 2016). It was found that the stiffness of PP increased by 67% when PP was reinforced with MPS treated hemp fibres, and by only 30% when PP was reinforced with untreated hemp fibres (Panaitescu et al. 2016). The improvement in the mechanical properties of hemp fibre reinforced composites after silane treatment was mainly due to the increased wettability of hemp fibres by polymers after silane treatment.

Besides silanes, other functional molecules have been used in fibre surface modification for improving wettability of hemp fibres by hydrophobic polymers. In previous studies, a combination of 1, 6- diisocyanatohexane (DIH) and 2-hydroxyethyl acrylate (HEA) was used to modify hemp fibre surfaces, and significantly increased tensile strength, flexural modulus of rupture (MOR), and flexural modulus of elasticity (MOE) have been achieved in hemp fibre reinforced unsaturated polyester composites (Qiu et al. 2011). The highest tensile strength of 65 MPa was obtained in composites made from 3% DIH combined with 2% HEA treated hemp fibres (Qiu et al. 2011). The highest MOR of approx. 110 MPa and MOE of approx. 7.8 GPa were obtained in composites made from 2% DIH combined with 1.4% HEA treated hemp fibres (Qiu et al. 2011). Besides using DIH and HEA, grafting *N*-methylol acrylamide (NMA) onto fibre surfaces in the presence of sulfuric acid as a catalyst has been found to increase tensile strength, MOR and MOE of hemp fibre reinforced unsaturated polyester composites (Qiu et al. 2012). Treatment of hemp fibres with 3% (w/w) of NMA increased the tensile strength, flexural strength and flexural modulus of composites by 42.0%, 92.9%, and 158.6%, respectively, when compared with untreated hemp fibre reinforced composites (Qiu et al. 2012).

Other coupling agents such as isocyanatoethyl methacrylate (IEM) have also been tested in hemp fibre surface modification (Chen et al. 2013). IEM is a heterofunctional monomer with a reactive isocyanate group and a vinyl polymerizable double bond, and the two function groups can react independently with other amorphous hydroxyl groups or vinyl monomers on the fibre surface respectively (Thomas 1983). Increased interfacial adhesion was observed from SEM graphs of tensile-fractured surfaces of hemp unsaturated polyester composites, as evidenced by fewer pull-out holes observed on the fractured surface of the composites with IEM treated hemp fibres (Chen et al. 2013). For the

549 mechanical properties of composites with hemp fibres treated at varied concentrations of IEM, the optimum treatment
550 was 3% (w/w) IEM for hemp fibres in terms of tensile strength (105 MPa), flexural strength (150 MPa) and flexural
551 modulus (10 GPa).

552 The grafting reactions discussed above have usually been conducted in the presence of chemical catalysts (e.g.
553 dibutyltin dilaurate for IEM treatment, and sulfuric acid for NMA treatment) or at acidic conditions (e.g. pH 4 – 5 for
554 silane treatment). Recently, grafting of non-polar polymers onto fibre surfaces using laccase catalyzed oxidation has
555 been demonstrated (Fan et al. 2012; Ni et al. 2015). Laccase catalysis can induce grafting of phenolic monomers onto
556 hemp fibre surfaces through phenoxy radical generation by catalytic oxidation of hydroxyl groups (Fan et al. 2012).
557 When hydroquinone was used as phenolic monomers during laccase treatment of hemp fibres, tensile strength of hemp
558 fibre reinforced polylactide acid (PLA) composites increased to 19 MPa from 13 MPa after laccase treatment (Fan et al.
559 2012). Enzyme catalyzed grafting can be done at low temperature and at pH values close to neutral which minimizes
560 the negative effect of natural fibres. It can be expected that laccase-catalyzed modification on natural fibre surfaces will
561 attract more attention in the future.

562 **5.3.4. Physical treatment**

563 Physical treatment of natural fibres using corona, UV, plasma or gamma radiation can change structural and surface
564 properties of the fibres and thereby influence the mechanical bonding between fibres and matrix polymers.

565 Corona treatment is a physical surface modification technique that uses low temperature corona discharge plasma to
566 oxidize fibre surfaces and impart changes in the surface properties. Corona treatment could result in a surface oxidation
567 and etching effect, leading to an improvement of the interfacial compatibility between fibres and matrix polymers
568 (Faruk et al. 2012). The corona plasma is generated by supplying a low frequency high voltage to electrodes that usually
569 have sharp tips (Ragoubi et al. 2010). Tensile strength of hemp fibre/PP composites increased to 38 MPa from 29 MPa
570 after hemp fibres were treated with corona discharge, and stiffness (refers toYoung's modulus or elastic modulus)
571 increased to 1215 MPa from 1079 MPa (Ragoubi et al. 2010). After corona treatment, increased interfacial bonding
572 between hemp fibres and polypropylene was achieved, as evidenced by fewer unbroken hemp fibres pulled out of the
573 fracture surfaces observed (Ragoubi et al. 2010). In general, modifications on hemp fibres by corona treatment include
574 increased surface roughness caused by the formation of micro-pits and cavities, which probably explained the improved
575 interfacial bonding between fibres and polypropylene (Ragoubi et al. 2010).

576 Ultraviolet (UV) light is known for its shorter wavelength and lower energy than visible light. Eposing natural fibres
577 to UV radiation has been widely used in natural fibre surface modification (Mukhopadhyay and Fangueiro 2009; Olaru

et al. 2016). UV light (preferably at wavelength of 185 and 254 nm) in the presence of oxygen generates atomic oxygen and ozone that results in the fibre surface being more hydrophilic (Zelez 1992). The behavior of hemp fibres when subjected to a hydrothermal pre-treatment followed by exposure to UV radiation (200 nm < wavelength < 700 nm, incident light intensity: 3.9×10^{-5} kW/cm^2) for 120 – 500 hours was assessed. It was found that UV radiation can affect the network of intra- and intermolecular hydrogen bonds and that there was a reduction of cellulose crystallinity caused by UV radiation treatment (Olaru et al. 2016). UV radiation treatment on other types of natural fibres such as jute fibres has also been carried out previously (Gassan and Gutowski 2000). In a study by Gassan et al. (Gassan and Gutowski 2000) tossa jute single fibres and fibre yarns were treated with UV radiation at a wavelength of 254 nm, which is the most important wavelength regarding generating atomic oxygen and ozone (Zelez 1992). The UV radiation treatment could lead to higher polarities (up to 200% increase) of the fibre surface, so that the wettability of the fibres by epoxy matrix was improved (Gassan and Gutowski 2000). Up to 30% increase in composite flexural strength has been achieved by UV treatment (Gassan and Gutowski 2000). In principle, increased polarity of fibres after UV treatment is disadvantageous for composite use especially when other hydrophobic polymers are used, while increased polarity of fibres probably benefits grafting co-polymerization and esterification and results in higher grafting efficiency and esterification efficiency.

Plasma treatment, especially cold plasma treatment, is another physical treatment to modify fibre surface without affecting the bulk properties of fibres, and is similar to corona treatment. Plasma treatment can be performed under vacuum and under atmospheric conditions (Mukhopadhyay and Fangueiro 2009). The hydrophilic nature of hemp fibres was found to be reduced by the etching effect of plasma, which was presumably due to migration of hydrophobic compounds from the fibre bulk to the surface (Baltazar-Y-Jimenez and Bismarck 2007). Increased hydrophobicity of the fibre surface is favorable for the mechanical performance of hemp fibre reinforced composites.

Gamma rays are packets of high-frequency electromagnetic energy and have been also used for natural fibre surface modification. Olaru et al. studied the changes in structure of hemp fibres after hydrothermal pre-treatment followed by gamma radiation, and found a 25 kGy dose gamma irradiation resulted in an increase of the crystallinity to 71.5% from 64% for control samples (Olaru et al. 2016). Interfacial bonding increased between pineapple leaf fibre/jute fibre and bisphenol-A matrix polymers in the hybrid composites after pineapple leaf fibres/jute fibres were exposed to gamma radiation with 5 kGy radiation dosage. The flexural strength of the hybrid composites increased from 33 MPa to 57 MPa and the impact strength of the composites increased from 2.5 KJ/m^2 to 3.0 KJ/m^2 (Raghavendra et al. 2015).

606 ## 5.4. Moisture uptake minimization

607 The hydrophilic nature of cellulosic fibres not only makes them less compatible with commonly used polymers,
608 which are usually hydrophobic, but also makes them vulnerable to moisture and biological contamination. When natural
609 fibres are used as reinforcing agents in composites, polymers form a strong barrier against moisture and biological
610 activities and generally protect fibres from swelling and degradation. However, the matrix polymers can only slow the
611 moisture diffusion process. Sooner or later (e.g. up to several months), moisture will penetrate through the polymer
612 matrix and contact fibres and cause fibre swelling, leading to decrease in mechanical properties of the composites
613 (Dhakal et al. 2007; Christian and Billington 2012). A major restriction in the successful use of natural fibres in durable
614 polymer composite applications is that the moisture absorption causes physical property changes, especially fibre
615 dimensions change. In addition moisture absorption may introduce delamination and defects at interfaces, which make
616 natural fibres less favorable competitors of synthetic fibres for long-term performance and durability applications
617 (Baltazar-Y-Jimenez and Bismarck 2007). Therefore, fibre pre-treatments are expected to prolong the duration of NFCs
618 and stabilize their mechanical properties by reducing the moisture effect. Many fibre treatments have been attempted to
619 increase water resistance ability of NFCs. Some treatments have been shown to be efficient in minimizing natural fibre
620 moisture uptake, such as hydrothermal treatment (Rouison et al. 2005) and chemical modification of fibre surface (Alix
621 et al. 2009; Chen et al. 2013).

622 In natural fibres, pectic substances and hemicelluloses of fibres, along with other cell wall components, are the
623 primary components contributing to surface hydrophilicity (George et al. 2016) which leads to moisture absorption, as
624 indicated by the relative moisture absorption propensity shown in Table 8. Therefore the removal of the components
625 which are more inclined to absorb moisture can improve moisture resistance of natural fibres. George et al (George et
626 al. 2016) reported that the removal of pectin and hemicellulose was found to improve moisture resistance of resulting
627 hemp fibre reinforced polypropylene (PP) composites. All investigated enzymatic treatments using xylanase (Xyl),
628 polygalacturonase (PG), laccase (Lac) and a combination of xylanase and cellulase (Xyl + Cel) were shown to decrease
629 moisture uptake of the resulting fibre reinforced composites relative to untreated fibre reinforced composite. Xyl + Cel
630 and PG treatments provided the greatest reduction in moisture uptake (less than 0.6% after immersion in water for 4
631 weeks) for hemp fibre reinforced PP composites.

632 Bismarck et al. attempted to understand the moisture absorption behavior of hemp fibres by measuring ζ-potential of
633 fibres using 1 mM KCl after exposure to 100% humidity for varied durations, namely the time-dependence of the ζ-
634 potential (i.e. ζ-potential =f(t)) (Bismarck et al. 2002). The ζ-potential measurements could clearly differentiate the

degree of hydrophilicity of the natural fibres. The untreated hemp fibres are the most hydrophobic due to presence of the highest amount of waxy substances on fibre surfaces, whereas the retting process decreased the water resistance ability of hemp fibres through the removal of those hydrophobic coverings during retting (Bismarck et al. 2002). As regards flax fibres, it was found the commercially available autoclave-treated (Duralin® process) fibres are more hydrophobic than the original flax fibres. In this hydrothermal treatment, a primary depolymerization of hemicellulose and lignin occurs after 30 min hydrothermal pre-treatment at 160 °C. Then, the aldehyde and phenolic functionalities are chemically grafted onto fibre surfaces by the post-curing at 150 °C (Alix et al. 2014). Duralin® fibres were thus found to have lower water uptake (approx. 18%) than untreated fibres (up to 43%) (Bismarck et al. 2002). Besides Duralin® process, traditional autoclave treatment at mild conditions (i.e. 0, 0.5 and 1 bar) was found to increase water resistance of natural fibres due to modification of fibre surfaces at low operating pressures, and at elevated operating pressures internal fibre structures were altered through removal of pectins (Alix et al. 2014).

Fibre surface modification by grafting hydrophobic chemicals or short polymers has been a commonly used method to reduce hydrophilic features of natural fibres. Qiu et al. grafted *N*-methylol acrylamide (NMA) in the presence of sulfuric acid as catalyst onto hemp fibre surfaces. They found that the water uptake of the resulting fibres was significantly decreased to 17% after fibres were treated with 10% (w/w) NMA compared to 22% for control samples. In another study, Qiu et al. (Qiu et al. 2011) treated hemp fibres with a combination of 1,6-diisocyanatohexane (DIH) and 2-hydroxyethyl acrylate (HEA) and achieved increased water resistance of the resulting hemp/unsaturated polyester (UPE) composites. For all investigated composite specimens, it took approx. 12 days for moisture diffusion to reach the equilibrium, as indicated by the changes in water uptake of the composite specimens. However, composites made with DIH-HEA treated fibres had significantly lower maximum water uptake (16 – 18%) than the composites made with untreated fibres (approx. 22%), and water uptake tended to decrease with the increase in the concentration of DIH (0 – 5%, wt %) and HEA (0 – 3.5%, wt %) used for fibre treatments (Qiu et al. 2011).

5.5. Anti-microbial degradation

As discussed above, natural fibres are sensitive to biological degradation, which is another restriction on the successful use of natural fibres in durable polymer composite applications. The degradation of cellulosic fibres by microorganisms in nature is usually accompanied with moisture uptake, or results inevitably after natural fibres have absorbed a high amount of moisture. The increase in moisture resistance of natural fibres in turn will also protect them from biological degradation. In principal, the methods discussed in Section 5.4 can not only improve moisture resistant of natural fibres, but also increase their ability to resist microbial degradation.

Pectin and hemicellulose are due to their moisture uptake propensity the most sensitive components to biological degradation, as indicated by the biological degradation propensity shown in Table 8. In principle, the removal of those components can lead to increased resistance to microbial degradation. Furthermore, such modifications of the fibre surface have long been applied to wood and some plant fibres to improve dimensional stability and environmental degradation resistance (Pott 2002). Hill et al. attempted to improve the resistance of NFCs to microbiological decay by acetylation treatment of natural fibres (e.g. coir, flax and jute fibres) (Hill et al. 1998): Both unsterile soil and vermiculite soil-layer tests were employed to determine the bio-resistance of chemically modified fibres (Hill et al. 1998). In microbiological decay tests, it was found that modified fibres exhibited a high degree of decay resistance in both tests over a 5 month test period, whereas control samples failed in less than 1 month (Hill et al. 1998).

6. NFCs application

6.1. Durability of NFCs

Durability may be defined as "capable of lasting" or "not transitory". In the context of engineering materials, durability would normally address resistance to degradation by chemicals (especially liquid water and moisture vapour), biota or stress (especially creep and fatigue) or combinations of those factors (e.g. environmental fatigue). For metals the resistance to chemicals is designated as resistance to corrosion, but for polymer composites the appropriate terms would be degradation or deterioration. The durability of reinforced plastics has been reviewed by Pritchard (Pritchard 1998), Schutte (Schutte 1994) and Liao et al (Liao et al. 1998). Maxwell et al (Maxwell et al. 2005) have reviewed accelerated ageing methods and lifetime prediction techniques for polymeric materials. For predicting suitability of a material over the complete lifetime of components Highly Accelerated Life Testing (HALT) can be used. Degradation mechanisms normally occur faster at higher temperatures, but if there is a change in the mechanism involved, then the data obtained may be misleading. ASTM D5229-92 recommends that HALT should only be conducted up to temperatures of 25°C below T_g (Standard 2014).

However, the above publications are primarily addressed to issues with synthetic fibre reinforced polymer matrix composites. Summerscales (Summerscales 2014) has considered the issues surrounding bio-based composites in wet conditions. Bajwa et al (Bajwa et al. 2015) have reviewed the impact of biofibres and coupling agents on the weathering characteristics of composites. A particular issue for composites in the marine environment is osmosis and blistering which leads to cosmetic and hydrodynamic damage, but to date no scientific literature on this topic has been identified.

At the macroscopic scale, the diffusion of gases, vapours or liquids into a material is normally modelled using Fick's law, with the fluid (e.g. moisture) content initially increasing with exposure time then approaching a saturation level.

693 For systems where sorption and/or reaction–diffusion produce a non-Fickian response, the diffusion coefficient can be
694 directly derived from sorption isotherms such as Henry's or Langmuir's laws (Verdu and Colin 2012).
695 Derrien and Gilormini (DG) (Derrien and Gilormini 2009) have presented a model for the time-dependent evolution
696 of the moisture content during unidirectional diffusion in a polymer submitted to hydrostatic load. Jacquemin and
697 Fréour (JF) (Jacquemin and Fréour 2012) presented two multiphysics models (a thermodynamic approach and a free
698 volume theory) for the effects of plasticization during water sorption and the internal mechanical state profile at both
699 constituent and ply scales. Discrepancies between the DG and JF models were found to increase significantly with the
700 coefficient of moisture expansion (CME). Perreux (Perreux 2012) presented a general behavior model to account for
701 time-dependent mechanical and environmental (water) loading of laminates and the induced damage. The first-stage
702 micro-mesomodel describes the variation in stiffness due to microcracks. The second stage kinetic model is based on
703 the thermodynamic definition of the forces driving damage and other dissipation potentials.
704 Osmosis is the process by which solution strengths are equalized by passage of the solvent (usually water) through a
705 semi-permeable membrane. In fibre-reinforced composites, the polymer matrix can act as the membrane. As water
706 diffuses through the polymer, any soluble solid material can dissolve and thus form a strong solution. Water will then
707 diffuse to this solution until the concentration gradient is reduced to zero. The volume of the solution will increase with
708 dilution and exert pressure on the surrounding material. When the stresses exceed a critical level, delamination will
709 occur (normally at the gelcoat-laminate interface) and will be manifest as blisters on the surface of the laminate. A
710 comprehensive list of chemical factors implicated in osmosis and blistering and other measures to reduce or eliminate
711 the problem are given in (Searle and Summerscales 1999).
712 A potential problem with natural fibre-reinforced polymer matrix composites is the hydrophilic nature of the ligno-
713 cellulose fibres and hence the moisture sensitivity of the resulting composites. Embedding the hydrophilic fibres in a
714 hydrophobic matrix will delay the absorption of water but diffusion and damage may compromise the material over
715 extended periods of time. Moisture will induce dimensional changes (swelling), mechanical performance changes
716 (plasticization and hence higher strains to failure but lower moduli) and higher susceptibility to microbiological attack.
717 Costa and D'Almeida (Costa and D'Almeida 1999) studied the effect of water absorption on the flexural properties
718 of jute or sisal fibre reinforced polyester or epoxy matrix composites. The diffusion behavior in both composites could
719 be described by the Fickian model. The jute-epoxy composites showed the best mechanical properties for all immersion
720 times studied. This behavior was attributed to better fibre–matrix interface integrity with epoxy resin and better
721 moisture resistance of the jute fibres (Costa and D'Almeida 1999).

Shah et al. (Shah et al. 2012; Shah et al. 2013) have recently presented fatigue life evaluations for aligned plant fibre composites through S–N curves and constant-life diagrams. The normalized fatigue performance (the fatigue strength exponent, b, defined by the stress intercept at twice the number of load reversals to failure) of the natural fibre composites was found to lie between that of glass-fibre and carbon-fibre reinforced composites.

There is increasing interest in the use of bio-based and/or biodegradable thermoplastic polymers or thermosetting resins as the matrix for composites with varying proportions of precursor materials extracted from plants (see e.g. (Summerscales and Grove 2013)). Ishimaru et al. (Ishimaru et al. 2012) reported that polycaprolactone, polyhydroxyalkanoate and polylactide thermoplastics or their copolymers (amongst others) have been applied as self-polishing/exfoliating matrices for controlled release of antifouling compositions. They conducted experiments which showed that barnacle settlement was significantly reduced by the slow release of low molecular weight poly (L-lactic acid) (PLLA without antifoulant chemical) in natural seawater.

6.2. Application of NFCs

NFCs are used in various applications nowadays. They are used in internal components in the automotive industry, e.g. kenaf/PLA spare tyre cover for Toyota Raum (2003) (Zini and Scandola 2011), dashboards, armrests and seat components (Daimler Chrysler) (Shuda et al. 2008), door linings and panels (BMW) (Holbery and Houston 2006; Shuda et al. 2008), door panel inserts and package trays (Opel) (Shuda et al. 2008), door panels (Ford) (Shuda et al. 2008) and floor trays (Faruk et al. 2014), pillar panels and central consoles (Volvo) (Faruk et al. 2014). Other automotive applications include boot (US trunk) liners, door cassettes, parcel shelves, and head restraints (Faruk et al. 2014). The high damping characteristics of NFCs will be appropriate for noise, vibration and harshness (NVH) suppression in all transport vehicles, such as noise insulation panels (Faruk et al. 2014). Applications on exterior panels of vehicles may be compromised by the moisture sensitivity of the respective composite components. It has been shown that natural fibres are a potential replacement for synthetic fibres in composite brake pads (Chand and Fahim 2008). In the construction industry, natural fibre biocomposites are being considered for hand rails, parquet flooring, slabs and window frames (Staiger and Tucker 2008). Amongst electronic applications, NEC developed a kenaf/PLA mobile phone outer casing in 2006 (Staiger and Tucker 2008).

Although there are challenges in making composites suitable for the marine environment, especially for vessels which remain afloat at all times, there have been a number of demonstrator applications. In the aerospace industry, the most likely first applications would be to exploit the high specific stiffness of composites in in-cabin components such as seats and luggage lockers, provided the flame, smoke and toxicity (FST) requirements can be met. Other high-value

applications might include biomedical and funeral articles, furniture, instrument cases and packaging (Zini and Scandola 2011). In the future, NFCs will see significantly increased use in structural applications when issues that limit successful use of natural fibres in composites have been solved.

7. Perspectives of natural fibre pre-treatment for composite use

Most fibre pre-treatment methods discussed above are chemical reaction-based methods, while more use of enzymes, especially oxidases e.g. laccases, for fibre pre-treatment is emerging. Those enzymatic fibre pre-treatment methods are environmentally friendly and more targeted for fibre treatment or surface modification. However, the mechanisms behind enzymatic reactions involving solid substrates (i.e. plant fibres) during fibre treatments are not fully understood. Therefore further work is still needed to improve understanding of how enzymes modify plant fibres to optimize those enzyme treatments and to develop more targeted methods.

Furthermore, the most widely used plant fibres for NFCs are bast fibres of plant such as hemp and flax because these bast fibres are strong and long. The long fibres could be easily aligned to make fibre orientation more uniform during composite processing. However, the cellulosic rich fibres from other lignocellulosic materials (e.g. wheat bran and wheat straw) are rather short and the short fibres limit their applications in producing strong NFCs. Therefore a continuous form of reinforcement agents (sliver, yarn, filaments) is needed from various sources of lignocellulosic materials for producing strong biocomposites in industrial use.

Studies are emerging on how to produce continuous form of filaments (also called regenerated fibres) using ionic liquids as dissolution solvent (Ma et al. 2015; Michud et al. 2015). Ionic liquids (ILs) have some unique, advantageous properties such as low toxicity, low evaporation and high thermal stability. More importantly, ILs have a high cellulose solubility at moderate conditions. This characteristic provides a useful tool to reshape and modify the components and properties of the resulting filaments. It has been shown that regenerated filaments with high tensile strength up to 800 MPa can be achieved with pure cellulose under optimum operating conditions using dry-jet-wet spinning (Ma et al. 2015). However, the surface properties of these regenerated fibres have not been intensively studied and little information is available currently. If the regenerated fibres need to be pre-treated prior to being used as reinforcing agents in composites, most of above discussed surface modification methods can in principle be applied to these fibres because the chemical composition of those natural plant fibres and regenerated plant fibres are more or less similar.

8. Conclusions

Many attempts have been made to use natural plant fibres in polymer reinforced composite materials. Improved mechanical performance and durability of NFCs have been achieved via improved fibre cultivation, fibre selection, fibre extraction, fibre treatments, and fibre surface modification methods. This paper has reviewed the research that has focused on improved short and long term mechanical properties and durability of NFCs containing natural fibres, notably differently pre-treated hemp fibres, focusing on improved interfacial bonding between fibres and matrix polymers and decreased hydrophilic features of fibres resulting from different fibre pre-treatments. Currently, many novel fibre pretreatment strategies and surface modification methods are chemically based methods, while research on use of enzymes, especially pectinases and oxidases e.g. laccases, for plant fibre pre-treatment and surface modification are emerging. Future research is still needed to expedite the application of NFCs and extend their durability and to improve their long-term performance including improvement of moisture resistance and microbial resistance by development of new targeted and environmentally friendly fibre pre-treatment methods.

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Figures

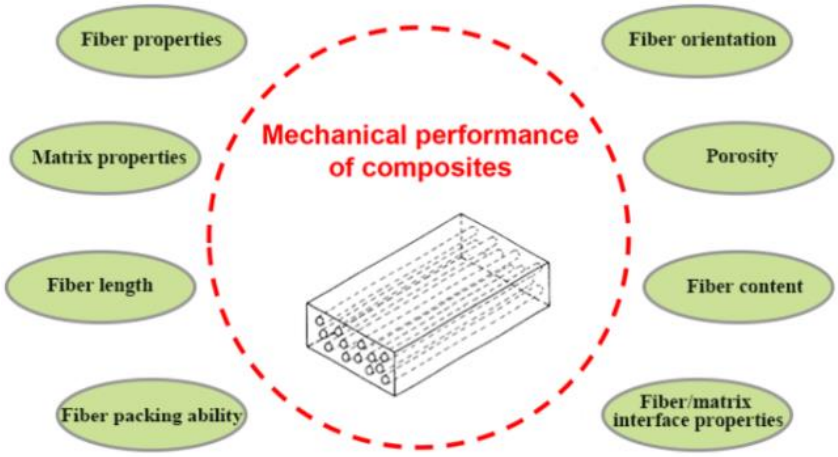


Figure 1. The performance of composites with fibres in a polymer matrix is governed by a range of parameters.

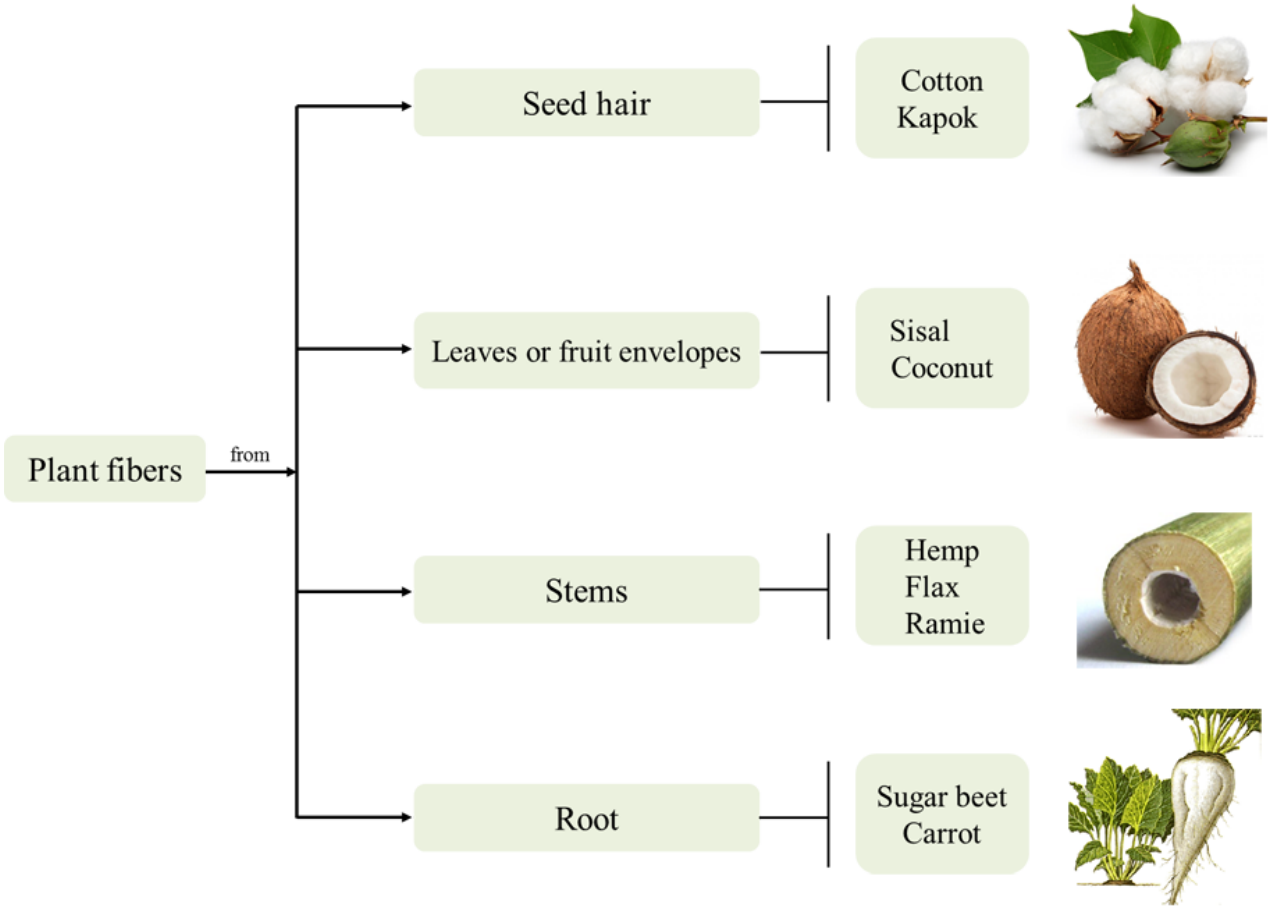
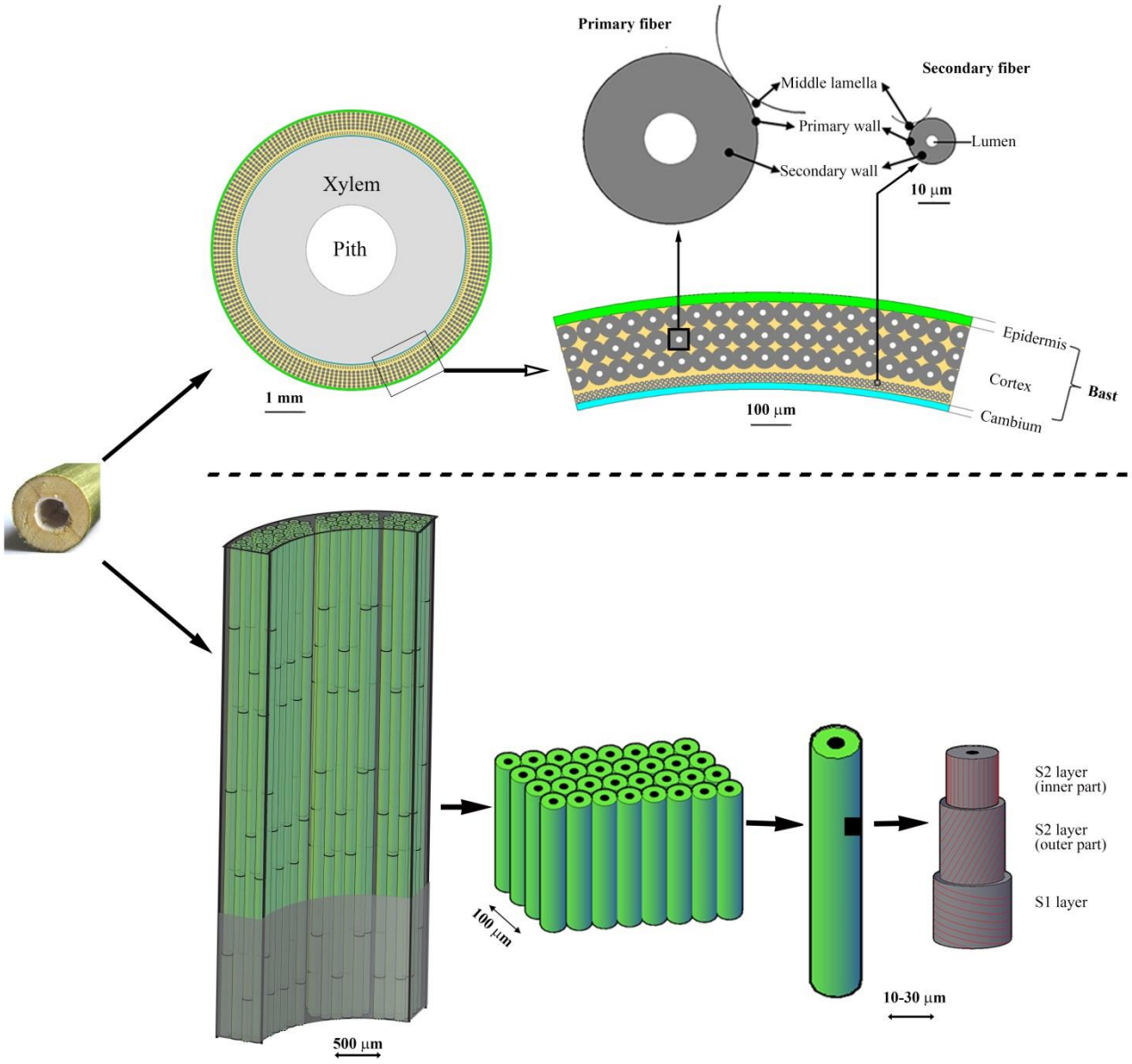


Figure 2. Classification of plant fibres according to their location in the plant.



1221

1222 **Figure 3.** Schematic diagram of a transverse section of hemp stem showing the organization and morphology of a bast

1223 strip and single fibre (e.g. primary- and secondary fibres) in the bast layer at different levels.

1224

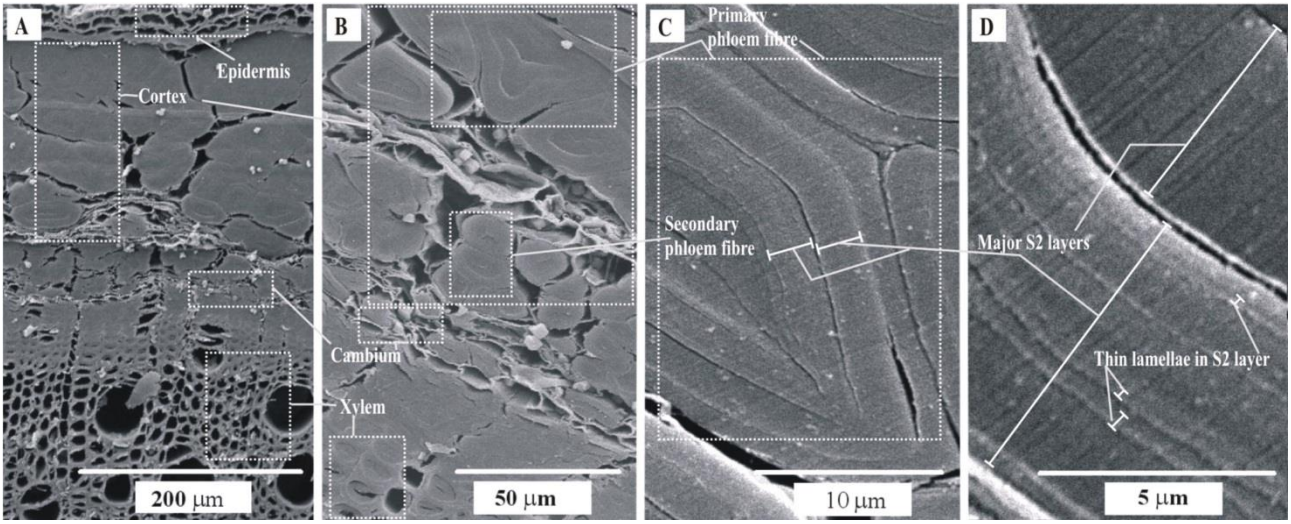


Figure 4. Hemp stem shown at increasing magnification using different transverse sections in SEM. A: Xylem + cambium + cortex + epidermis; B: Primary and secondary single fibres; C: Major layers in primary single fibre; D: Thin lamellae within the S2 layer (above) and a model of the microfibril orientation throughout the secondary cell wall (below) (Thygesen et al. 2006).

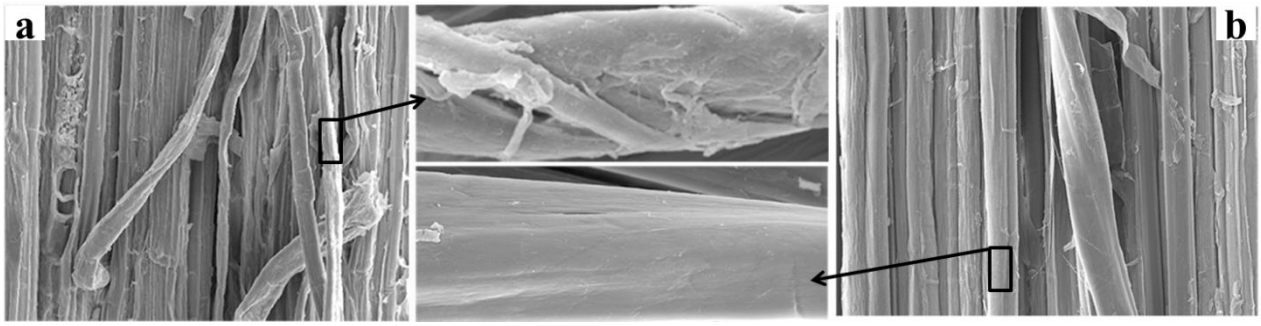


Figure 5. SEM micrographs of 0.5% EDTA + 0.2% endopolygalacturonase (EPG) treated fibres (a) and 0.5% EDTA + 0.2% EPG followed by 10% NaOH treated fibres (b) (——— 50 µm for images a and b).

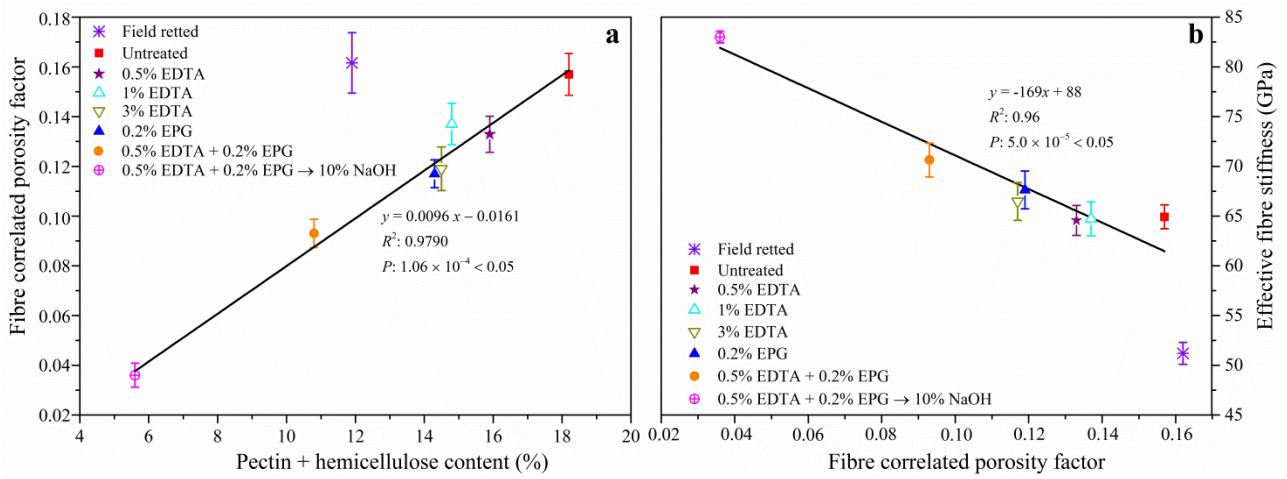


Figure 6. Fibre correlated porosity factor versus pectin + hemicellulose content (a) and effective fibre stiffness versus fibre correlated porosity factor (b) (Liu et al. 2016b).

Tables

Table 1. Desirable properties for fibres to be used as reinforcement agents in unidirectional fiber reinforced composites.

➢ High stiffness and strength
➢ Little scatter in mechanical properties
➢ Long and continuous form of fibres with high specific surface
➢ Low moisture uptake/high moisture resistance
➢ Hydrophobic and smooth fibre surface
➢ Little or no deformation due to changes in temperature or moisture
➢ Other properties e.g. high thermal stability, anti-microbial degradation/microbial decay resistance

1244 **Table 2.** Advantages and disadvantages of NFCs (Oksman et al. 2003; Faruk et al. 2012; Pickering et al. 2015)
1245 compared to glass fibre reinforced composites.

Advantages	Disadvantages
➢ Production of natural fibres is perceived to have low environmental impact	➢ Lower durability than synthetic fibre composites, but durability can be improved with fibre treatments
➢ High specific stiffness and strength	➢ High moisture absorption can result in fibre swelling
➢ Low density	➢ Lower strength and stiffness than synthetic fibres
➢ Lower fibre production costs than synthetic fibres	➢ Considerably higher variability in properties of fibres
➢ Low hazard manufacturing process	➢ Lower thermal stability
➢ Low emission of toxic fumes when subjected to heat and during incineration at the end of life	➢ Less stable when subjected to natural microorganisms because cellulose fibres are biodegradable
➢ High possibility for modifying fibre surface and structure	➢ Hydrophilic fibre surface reduces fibre/matrix interface properties
➢ Composting at end-of-life	➢ Supply chain issues for fibres harvested in the temperate zone

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1248 **Table 3** Chemical composition of hemp fibres from different cultivars (hemicellulose refers to pentosans in hemp
1249 fibres)

Cultivar	Cellulose (%)	Hemicellulose (%)	Pectin (%)	Lignin (%)	Reference
USO31	78.4-81.7	5.7-6.4	-	10-13	(Jankauskiene et al. 2015)
Unspecified	58.7	14.2	16.8	6	(Le Troedec et al. 2008)
Fedora 17	65.6-84.9	6.0-8.1	9.4-25	2.7-4.5	(Crônier et al. 2005)
Felina	57.1-61.8	8.3-14.3	2.8-8.6	1.2-7.3	(Thygesen et al. 2002)
Unspecified	76.1-89.2	1.9-12.3	-	2.1-5.7	(Kostic et al. 2008)
Unspecified	82.0-88.9	4.1-8.4	-	2.2-3.8	(Di Candilo et al. 2010)
Unspecified	88.3-91.0	6.5-9.8	-	1.4-2.1	(Madsen et al. 2007b)
Felina 34	64.0-83.0	11.0-15.0	1.0-6.0	1.0-4.0	(Thygesen et al. 2007)
USO	54.4	-	8.7	6.1	(Pakarinen et al. 2012)
Fedora	55	16	8	4	(Bonatti et al. 2004)
Felina	64-76	15	1-6	2-4	(Thygesen et al. 2006)
Unspecified	53.9-57.6	16.3-18.2	6.5-7.1	20-21	(Zhang et al. 2014)
Fibrimon 56	53.2	6.9	-	5.0	(van der Werf et al. 1994)
Fedora 19	58.6	9.3	-	5.0	(van der Werf et al. 1994)
Kompolti Sárgaszárú	68.2-69.2	6.7-8.5	-	3.5-5.5	(van der Werf et al. 1994)
Kompolti Hybrid TC	60.2-74.3	7.1-7.9	-	3.3-4.4	(van der Werf et al. 1994)
Unspecified	63.7-78.4	11.8-17.3	1.9-7.3	1.7-5.0	(Thygesen et al. 2011)

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1252 **Table 4** Mechanical properties of hemp fibre and synthetic fibre.

Fibre type	Density (g/cm^3)	Tensile strength (MPa)	Stiffness (GPa)	Failure strain (%)	Reference
Hemp	1.4-1.5	550-600	25-35	-	(Sawpan et al. 2011a)
Hemp	1.5	310-750	30-60	2-4	(Mwaikambo and Ansell 2006)
Hemp		368-482	17.6-19.6	2.5-3	(Duval et al. 2011)
Hemp		889 ± 472	35.5 ± 17.3	2.6 ± 2.2	(Marrot et al. 2013)
Hemp		699 ± 450	31.2 ± 19.7	3.3 ± 1.6	(Marrot et al. 2013)
Hemp		489 ± 233	33.8 ± 12.2	2.5 ± 1.3	(Marrot et al. 2013)
Hemp		857 ± 260	58	-	(Pickering et al. 2007)
Hemp		886	66	-	(Fan et al. 2011)
Hemp		636 ± 253	27.6 ± 7.5	2.1 ± 0.7	(Placet et al. 2012)
Hemp	1.6	200-1000	-		(Thygesen et al. 2011)
Glass fibre	2.55	1956	79	-	(Fu et al. 2000)
Carbon fibre	1.30	3950	238	-	(Fu et al. 2000)

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1255 **Table 5** Properties of commonly used thermoplastics in NFCs.

Thermoplastics	T_m* (°C)	Density** (g/cm^3)	Stiffness (GPa)	Tensile strength (MPa)	Elongation (%)	References	Example used in NFCs
Polyester	/	1.2	4	61	2.5	(Brahim and Cheikh 2007)	(Aziz and Ansell 2004; Seki et al. 2010)
High density polyethylene (HDPE)	130	0.96	1.0 – 1.1	22 – 31	10 − 1200	(Stevens 1999; Deanin and Mead 2007; Lerche et al. 2014)	(Pucciariello et al. 2004; Lu and Oza 2013)
Low density polyethylene (LDPE)	108	0.92	0.2−0.3	8.3 – 31	100 – 650	(Stevens 1999; Deanin and Mead 2007)	(Pucciariello et al. 2004; Madsen et al. 2007a; Prasad et al. 2016)
Polystyrene (PS)	84 – 106	1.04 – 1.06	2.3 – 3.3	36 – 52	1.2 – 2.5	(Stevens 1999; Deanin and Mead 2007)	(Pucciariello et al. 2004; Naik and Mishra 2006)
Poly(lactic acid) (PLA)	155 – 171	1.24	3.6	56 − 66	1.2 − 100	(Stevens 1999; Duc et al. 2014)	(Oksman et al. 2003; Yu et al. 2014)
Poly (vinyl chloride) (PVC)	199	1.35	2.4 – 4.1	41 – 52	40 – 80	(Stevens 1999; Rosato et al. 2000)	(Huang et al. 2012)
Polyamide (Nylon)	260	1.13	/	76 – 83	0.6 − 300	(Stevens 1999; Rosato et al. 2000)	(Bourmaud et al. 2016; Kiziltas et al. 2016)
Polyethyleneterephthalate (PET)	250	1.34	2.8 – 4.1	48 − 72	50 – 300	(Stevens 1999; Rosato et al. 2000)	(Madsen et al. 2007a)
Polypropylene (PP)	168	0.90	1.2 – 1.7	31 – 41	100 − 600	(Stevens 1999; Rosato et al. 2000)	(Madsen et al. 2007a)
Polycarbonate (PC)	266	1.20	2.4	66	110	(Stevens 1999; Rosato et al. 2000)	(Threepopnatkul et al. 2009)
Poly (methyl methacrylate) (PMMA)	95	1.20	2.2 – 3.2	48 − 76	2 − 10	(Stevens 1999; Rosato et al. 2000)	(John et al. 2015)

1256 * T_m- melting point of polymers. ** At room temperature.

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1258 **Table 6** Properties of commonly used thermosets in NFCs.

Thermosets	Curing temperature (°C)	Density* (g/cm^3)	Stiffness (GPa)	Tensile strength (MPa)	References	Example used in NFCs
Epoxy	80 − 150	1.1 – 1.3	2.7 – 4.1	55 − 130	(Crosky et al. 2014; Wang et al. 2015; Liu et al. 2016c)	(Liu et al. 2016b; Liu et al. 2016c)
Phenol-formaldehyde	100 − 185	1.6 – 1.2	0.38	10	(Hauptt and Sellers 1994; Sreekala et al. 2000)	(Sreekala et al. 2000; Nabihah et al. 2015)
Urea-formaldehyde	120 − 145	0.9 – 1.6	14	35	(Bliznakov et al. 2000; Osemeahon et al. 2007; Zhong et al. 2007; Singha and Thakur 2008; Singha and Thakur 2009)	(Zhong et al. 2007; Singha and Thakur 2008)
Polyester	65 − 80	1.2	0.6 – 3.6	20 − 80	(Sanadi et al. 1986; Pepper 2001; Baley et al. 2006; Crosky et al. 2014)	(Marais et al. 2005; Dhakal et al. 2007)
Melamine-formaldehyde	90 − 120	1.5	9	75	(Pekala et al. 1992; Voigt et al. 2003)	(Hagstrand and Oksman 2001)
Polyurethane	80 − 125	1.2	0.43	4.8	(Rozman et al. 2003; Saint-Michel et al. 2006; Bakare et al. 2010)	(Hufenbach et al. 2013)
Furan	40 − 90	1.3	3 − 8.5	30 − 60	(Eisenreich 2008; Džalto et al. 2014; Domínguez and Madsen 2015)	(Džalto et al. 2014)

1259 * At room temperature

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1261 **Table 7** Activities of different enzymes detected in hemp fibres treated by field retting and fungal retting (Liu et al.

1262 2016d).

Enzyme	Activity[1] (U/ g dry matter of hemp fibres)						Substrate[2]	Reference[3]
	Field retting duration (days)			Fungal retting duration (days)				
	7	14	20	7	14	20		
Glucanase	0.08	0.10	0.04	0.03	0.07	0.04	10 g/L carboxymethyl cellulose (CMC)	(Suwannarang see et al. 2014)
Polygalacturonase	0.04	0.02	0.06	0.60	0.29	0.12	2 g/L polygalacturonic acid	(Thomassen et al. 2011)
Galactanase	0.11	0.11	0.10	0.70	2.74	0.04	5 g/L potato galactan	(Michalak et al. 2012)
XG-specific endoglucanase	0.01	0.08	0.01	0.19	0.32	0.30	10 g/L tamarind xyloglucan	(Benko et al. 2008)
Laccase	0	0	0	0.41	0.48	0.95	0.5 mM ABTS	(Li et al. 2008)

1263 [1] The activity of glucanase, polygalacturonase, galactanase and XG-specific endoglucanase: one unit of activity is

1264 defined as the volume of crude enzyme extracts (µL) required to liberate 1 µmole reducing ends (glucose equivalents)

1265 per minute under assay conditions. The activity of laccase: one unit of activity is defined as the volume of crude enzyme

1266 extracts (µL) required to oxidize 1 µmol ABTS per minute under assay conditions.

1267 [2]ABTS – 2,2-azinobis (3-enthylbenzthiazoline)-6 sulphonate.

1268 3 Reference for methods used for enzyme activity assay in Liu et al. (Liu et al. 2016d).

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1270 **Table 8** Cell wall components of natural fibres responsible for moisture uptake and biological degradation (adapted
1271 from Mohanty A.K. Misra M 2000).

Component	Moisture uptake	Biological degradation
Hemicellulose	+ + + + + + + +	+ + + + + + + + + + + +
Accessible crystalline cellulose	+ + + + + +	+ + + + + + + + +
Non-crystalline cellulose	+ + +	+ + + + + + + +
Crystalline cellulose	+ +	+ + + + +
Lignin	+	+

1272 * "+" indicates propensity to moisture uptake or to biological degradation.

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